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Abstract
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Photoemission studies of the γ-α phase transition in Ce: Changes in $4f$ character

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Photoemission studies of the γ-α phase transition in cerium show changes in two $4f$-related features in the valence band (0.3 and 2 eV below E_F) and broadening of the multiplet structure in the region of the $4d$-$4f$ transitions. We show that the observed features can be explained by increased hybridization of the $4f$ wave function upon entering the α phase.

The γ-α phase transition in metallic cerium has been, and continues to be, of great interest because its understanding is so elusive.[1] The original interpretation was that the single, localized, $4f$ electron in γ-Ce was "promoted" to a conduction-electron state in the α phase. Subsequent experimental results have not been consistent with this view and additional work led to interpretations in which $4f$ delocalization[2] and valence-band hybridization were proposed. To examine these models for γ-α-Ce, we undertook a temperature-dependent photoemission experiment using synchrotron radiation.

Photoelectron spectroscopy has been previously used to study γ-Ce (Refs. 3 and 4) but the results have not been described adequately by either the promotion model or any model involving extensive radial wave-function expansion. In this Communication we show that the results can be explained by small changes in hybridization, the $4f$ becoming slightly less localized in α-Ce than in γ-Ce.

We report results from two complementary photoemission studies. The first emphasizes photoyield measurements in the region of the $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$ excitations. The exchange splitting of the excited $4d^9 4f^{n+1}$ states is large because the $4d$ and $4f$ radial wave functions overlap well, resulting in rich multiplet features. The number of multiplet structures and their relative energies are particularly sensitive to changes in either the $4f$ number or the $4f$ radial wave functions.[5–8] The second experiment emphasizes the valence-band photoemission spectra and shows that there are two $4f$-related features (binding energies 0.3 and 2 eV) which change in relative intensity at the γ-α phase transition. The results of these two experiments indicate that there is little change in the number and radial extent of the $4f$ electrons between the γ and α phases. The changes observed are consistent with a picture in which the changes occur primarily in the tails of the $4f$ wave function far from the cores and that these changes involve only a small fraction of the $4f$ charge.

The photoemission measurements used synchrotron radiation from the Tantalus electron storage ring at the University of Wisconsin for studies in the spectral range from 10 to 175 eV (toroidal grating and grasshopper monochromators). Photoemission spectra were taken using a commercial double-pass cylindrical mirror analyzer. In the yield measurements, photoelectrons with kinetic energies of 2–4 eV were counted as the photon energy was varied (monochromator resolution ~ 0.1 eV); these emphasize bulk properties because the measured electrons are those which have been inelastically scattered before escaping from the solid (estimated escape depth 30–50 Å).[9] For the valence-band studies, energy distribution curves (EDC's) were measured with a typical overall resolution of ~ 0.4 eV; these were inherently more surface-sensitive measurements. All measurements were conducted in a UHV spectrometer at an operating pressure of $\sim 5 \times 10^{-11}$ Torr. The samples were thick films evaporated *in situ* (tungsten basket, high purity electropolished Ames Laboratory Ce) at pressures never exceeding 2×10^{-10} Torr, with immediate recovery to operating pressures after deposition (~ 30 sec). Studies of the γ phase were made with films deposited onto room-temperature substrates; those in the α phase used films both cooled from room temperature to ~ 50 K and films deposited onto a substrate held at ~ 50 K with a closed cycle helium refrigerator.

The electrical resistance of the film was measured as a function of temperature. The phase transition produced a decrease in resistance upon cooling at ~ 100 K and an increase upon warming at ~ 160 K. The changes clearly indicate the formation of α-Ce, but the resistivity results were not as dramatic as

those obtained using single crystals.[1] The changes we observed in our photoemission results were more pronounced in the films evaporated at low temperature because this enhances the formation of α phase and diminishes the growth of other phases.[10]

In Fig. 1 we show yield spectra for γ- and α-Ce in the vicinity of the $4d$-$4f$ excitations. For comparison we show analogous results for CeF_3, a large gap ionic insulator in which the Ce^{3+} ions are surrounded by a cage of fluorine nearest neighbors and the $4f$ electrons are localized. Comparison of the multiplet structures calculated in an atomic model for tripositive rare-earth ions[5–8] with those observed for CeF_3 (Refs. 11–13) shows generally excellent agreement in the region of the fine structure (104–113 eV) and in the region of the three autoionization-broadened d-f channels near 125 eV, as indicated by vertical lines in Fig. 1.

The results in Fig. 1 provide extremely important indications of the nature of the $4f$ state in γ- and α-Ce. First, the multiplet structures are considerably broader in γ-Ce then in CeF_3 (see inset Fig. 1). This broadening is due to a slight hybridization of the $4f$ electrons with the $5d$ valence-band electrons. This wave-function mixing implies that the purely atomic model upon which the $4d$-$4f$ Ce multiplet calculations were based is not completely valid (spin and angular momentum are no longer rigorously valid quantum numbers and the $4f$ wave function is influenced by the solid-state environment).

Second, the multiplet features broaden even further at the phase transition indicating *increased 4f hybridization in* α-Ce. We interpret this broadening as due to f-d mixing as disucssed in the companion theory paper by Liu and Ho.[14] It is important to note

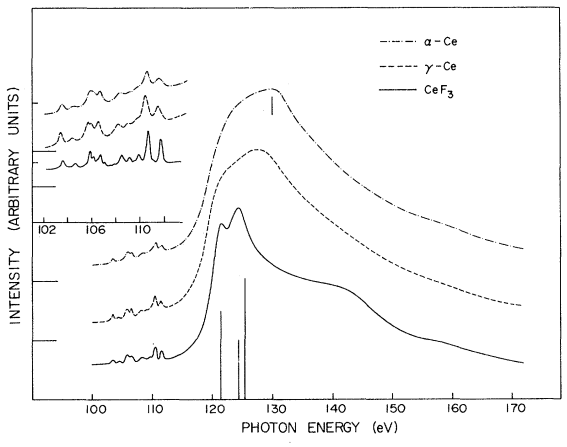

FIG. 1. Photoyield of CeF_3 (300 K), γ-Ce (300 K), and α-Ce (50 K) in the region of $4d$-$4f$ excitations. All curves are normalized to total area under each curve. The broadening of the multiplet fine structure (insert) is interpreted in terms of d-f hybridization.

that there are no new multiplet structures which appear in this region. The appearance of new structure would indicate a major change in electronic configuration toward the formal Ce^{4+} configuration and the loss of the $4f$ electron (f^0 or La^{3+}-like has only one major multiplet, a second weaker one, and the $^1P_1$ state which autoionizes). Since the promotion model would predict just this change, we can rule it out as a viable model. Furthermore, if the $4f$ wave function were to expand radially, the $4d$-$4f$ wave-function overlap would diminish and the resulting changes in the exchange intergrals would alter the splitting of the multiplet structure. That none is seen indicates the radial expansion of the $4f$ is not great.

Finally, changes occur in the yield spectra above 115 eV (Fig. 1). The calculated absorption spectrum for Ce^{3+} agrees well with that of CeF_3 but disagrees with that of either Ce vapor or Ce metal. Clearly the line shapes are influenced by details of the autoionization process and transitions to other parts of the conduction band. The changes at the phase transition near 130 eV (tic mark Fig. 1) may be due to at least two factors, neither of which can be quantified at this point. First, in view of the difference between the free ion (CeF_3) and the metal (γ-Ce), the 6% lattice contraction that accompanies the phase transition could have a significant effect. The lattice change has ramifications in the autionization process, other final-state changes, and possible interference effects on the outgoing electron. Secondly, studies of mixed-valence compounds[15,16] show that not only is the fine structure influenced by f count, but that there is also increased intensity at 130 eV. A shift of the valence towards 4+ is accompanied by the shift of the main peak to a single La^{3+}-like structure centered at 130 eV.[17] This suggests that the change in effective f count via the change in hybridization could also account for the observed changes through the many-body interaction.

This use of the $4d$-$4f$ multiplet structures to examine the atomic versus solid-state properties of the $4f$ wave function offers a unique way of gauging the $4f$ count. In CeF_3, these features are very sharp; in the $Ce(AgPd)_3$-$CeRh_3$ system,[16] the $4f$ count diminished precipitously; here in γ-α-Ce, we have clear evidence of a change in $4f$ mixing at the phase transition.

The valence-band spectra offer additional insight into $4f$ hybridization in γ-α-Ce. As has been shown in previous studies of Ce compounds,[16,18] there are two ways of highlighting the $4f$ character in the valence bands, namely, by identifying changes in valence-band EDC's taken at photon energies of ~ 30 and ~ 60 eV due to the dramatic decrease on the photoionization cross section of the $5d6s$ valence-band states compared to the $4f$ and by comparing EDC's at ~ 115 and ~ 120 eV to use the $4d \rightarrow 4f$ giant resonance to enhance the $4f$ features. In Fig. 2 we show EDC's for γ- and α-Ce measured

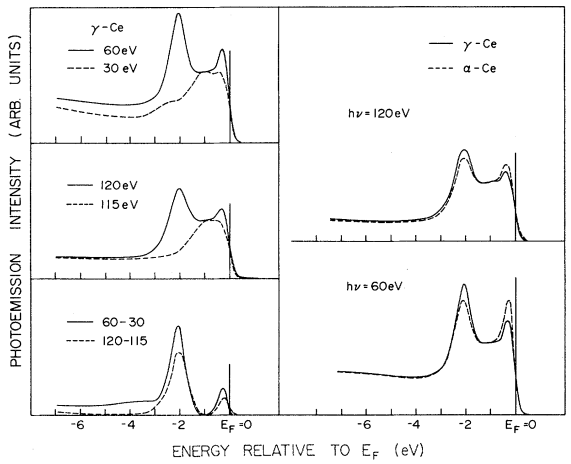

FIG. 2. Photoemission EDC's for α- and γ-Ce. Spectra on the left for γ-Ce highlight the $4f$ character through variations in d/f partial photionization cross sections (uppermost), through resonance photoemission, and through difference curves (lower most). Spectra on the right compare γ- to α-Ce using photon energies where the $4f$ character is most pronounced.

in both spectral ranges. On the left we show the spectra for γ-Ce comparing 30–60 and 115–120 eV; difference curves shown in the lower left portion of the figure. Both comparisons give the same important message: there are two spectral features which exhibit very nearly the same $h\nu$ dependence and resonance behavior.

We propose that the weaker structure at 0.3 eV reflects the excitation of a $4f$ electron with localization of a $5d$ screening orbital and "complete relaxation" of the system about the $4f$ hole. The deeper structure, which has been observed in other photoemission experiments,[3,4] represents the final state without screening and, as discussed by Liu and Ho,[14] the binding energy is very close to the energy of the f state, -2 eV. The latter is the "direct process" and the former arises from "shake-down" processes.

At the γ-α phase transition, we see from the right of Fig. 2 that the structure near E_F increases in α-Ce relative to that in γ-Ce and, conversely, the intensity of the deeper structure decreases. This is just what would be expected if the $4f$ electrons hybridize more in the α phase than in the γ phase (reduced d-f Coulomb repulsion). With increased coupling to valence-band electrons, screening becomes more likely and the intensity of the screened emission feature increases at the expense of the unscreened feature. Within our experimental uncertainty, there has been no change in the energies of either feature.

The picture we propose, in which the $4f$ electron hybridizes more in the α phase than in the γ phase, is consistent with previous positron annihilation[19] and Compton scattering[20] measurements and with recent muon spin rotation measurements.[21] These all have indicated that the valence-band density of states does not change precipitously at the phase transition and, like us, have found no evidence to support the promotion model. It is also consistent with the recent calculation of Pickett *et al.*[22] which showed that the $4f$ levels broaden at the phase transition because of increased overlap of the $4f$ wave-function tails. The observation of the many-body state near E_F represents a major step toward reconciling the results of diverse experiments including photoemission and the low-energy probes (e.g., susceptibilities).

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